

# Berry's phase for large spins in external fields

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It is shown that even for large spins  $J$  the fundamental difference between integer and half-integer spins persists. In a quasi-classical description this difference enters via Berry's connection. This general phenomenon is derived and illustrated for large spins confined to a plane by crystalline electric fields. Physical realizations are rare-earth Nickel Borocarbides. Magnetic moments for half-integer spin ( $\text{Dy}^{3+}$ ,  $J = 15/2$ ) and magnetic susceptibilities for integer spin ( $\text{Ho}^{3+}$ ,  $J = 8$ ) are calculated. Experiments are proposed to furnish evidence for the predicted fundamental difference.

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The common belief that large spins are equivalent to classical charged gyroscopes was strikingly undermined by Haldane<sup>1</sup> who indicated that the groundstate and low-lying states of magnetic chains consisting of localized spins  $J$  are different for integer and half-integer  $J$  even if  $J$  is large. Here we consider a similar effect for individual large spins placed in an external fields such as the crystalline electric field (CEF) and the external magnetic field. Its origin can be traced back to a geometric phase occurring on passing from quantum mechanical to quasi-classical spins.

The general Hamiltonian of a localized spin associated with a magnetic moment can be written as a function of its components:

$$H_S = \hat{f}(\vec{J}) - \vec{h} \cdot \vec{J} \quad (1)$$

where  $\hat{f}(\vec{J})$  is an arbitrary function of  $\vec{J}$  satisfying only two requirements: it is a Hermitian operator and it is an even function of  $\vec{J}$ :  $\hat{f}(\vec{J}) = \hat{f}(-\vec{J})$ . The latter requirement is equivalent to time-reversal symmetry<sup>2</sup>. In this paper we will focus on localized moments which are essentially confined to a plane. The confinement is due to the effects of the crystalline electric field. The important degree of freedom is rotation about the normal vector of a certain plane which we choose as  $z$ -direction. It is then appropriate to introduce the azimuthal angle  $\varphi$  and its conjugate momentum  $J_z$  as canonical variables. Setting  $\hbar = 1$  we may use

$$J_z = -i \frac{\partial}{\partial \varphi} \quad (2a)$$

$$J_x = \sqrt{J(J+1) - J_z^2} \cos \varphi \quad (2b)$$

$$J_y = \sqrt{J(J+1) - J_z^2} \sin \varphi. \quad (2c)$$

Eqs. (2) generally have a symbolical meaning since the operators on the right hand sides should be ordered to guarantee that  $J_x^+ = J_x$ ;  $J_y^+ = J_y$  and that the canonical permutation relations are satisfied. However, at large  $J$  the non-commutativity is small and we do not need to bother with the symmetrization. Inserting (2) into the Hamiltonian (1), the problem is reduced to the solution of a Schrödinger wave equation with, in general, a complicated differential operator.

So far, no difference between integer and half-integer spins occurred. The difference resides in a different global phase behavior. For large spins  $J$  one may pass to a quasi-classical description via the overcomplete set of coherent states  $\psi_{\vec{n}}$  with

$$\langle \psi_{\vec{n}} | \vec{J} | \psi_{\vec{n}} \rangle = J \vec{n}. \quad (3)$$

Moving the spin induces a certain orbit of the tips of the unit vectors  $\vec{n}$  on the unit sphere  $S^2$ . If this orbit is closed there is *no* difference in the purely classical picture between starting point and end point. Due to Berry's connection<sup>3</sup>, however, this is not the whole story. In order to be quantitative we first have to fix the phases of the  $\psi_{\vec{n}}$  in (3). The natural choice is to fix the phase of  $\psi_{\vec{z}}$  and to take<sup>4</sup>

$$\psi_{\vec{n}} = \exp(iJ_z \varphi) \exp(iJ_x \theta) \exp(-iJ_z \varphi) \psi_{\vec{z}} \quad (4)$$

where  $(\varphi, \theta)$  are the angles characterizing the unit vector  $\vec{n}$  ( $\vec{z}$  being the unit vector in  $z$ -direction). Berry's connection is given for the single, non-degenerate state  $\psi_{\vec{n}}$  (abelian case<sup>3,5,6</sup>) by  $\vec{A} = \langle \psi_{\vec{n}} | i \vec{\nabla} | \psi_{\vec{n}} \rangle$ . Since  $\vec{n}$  is confined to the unit sphere, spherical coordinates are most appropriate and only the  $A_\theta$  and the  $A_\varphi$  components matter. One finds

$$A_\theta = \langle \psi_{\vec{n}} | i \partial / (\partial \theta) | \psi_{\vec{n}} \rangle = -\langle \psi_{\vec{z}} | J_x | \psi_{\vec{z}} \rangle = 0 \quad (5a)$$

$$\begin{aligned} A_\varphi &= \langle \psi_{\vec{n}} | i \sin(\theta)^{-1} \partial / (\partial \varphi) | \psi_{\vec{n}} \rangle \\ &= \sin(\theta)^{-1} \langle \psi_{\vec{z}} | J_z (1 - \cos(\theta)) + \sin(\theta) J_y | \psi_{\vec{z}} \rangle \\ &= J(1 - \cos(\theta)) / \sin(\theta). \end{aligned} \quad (5b)$$

This connection then gives rise to the geometrical phase  $\exp(i \int_\gamma \vec{A} d\vec{l})$  along the path  $\gamma$ . Since we are interested in this work in motion in the  $xy$ -plane only, we have  $\theta = \pi/2$  and thus the phase is  $\exp(iJ\Delta\varphi)$ . As was to be expected from the physical origin of this phase it can be put to zero *locally* by an appropriate gauge. Globally, i.e. for complete tours of  $\Delta\varphi = 2\pi$ , one sees that no effect occurs for integer  $J$  but that for half-integer  $J$  a factor -1 applies

which cannot be gauged away. One way to account for the phase behavior is to use (2a) and *antiperiodic* boundary condition for half-integer spins and *periodic* boundary condition for integer spins, respectively. A more elegant way is to stick to the connection  $\vec{A}$ . This means we use

$$J_z = -i \left( \frac{\partial}{\partial \varphi} - iA_\varphi \right) \quad (6)$$

instead of (2a). Since, however, a change of gauge can alter  $A_\varphi$  by any integer value one may use (2a) for integer spins. For half-integer spins we use  $J_z = -i(\partial/(\partial\varphi) - i/2)$ .

Thus, despite of the large value of  $J$ , the low-lying states of the Hamiltonian (1) for integer and half-integer spins are fundamentally different. In the absence of an external magnetic field all stationary states of a half-integer spin are doubly degenerate (Kramers degeneracy<sup>7</sup>). This means that, in analogy to the linear Stark effect, the groundstate may be characterized by a finite magnetic moment. To the contrary, the groundstate of an integer spin is non-degenerate for sufficiently low crystalline symmetry. Therefore, the magnetization in the groundstate is exactly zero and depends linearly on the magnetic field as long as the field is weak enough.

To be more specific, we consider an important application of these general ideas to the ions of the rare earth elements  $\text{Ho}^{3+}$  and  $\text{Dy}^{3+}$ . The triply charged ions are decisive for the magnetic moments in the compounds  $R\text{Ni}_2\text{B}_2\text{C}$  ( $R$  stands for a rare earth element) the properties of which attracted much attention in the last few years<sup>8–11</sup>. The ion  $\text{Ho}^{3+}$  has 10 electrons in the 4f-shell. According to Hund's rule, it has the total spin  $S = 2$ , the orbital moment  $L = 6$  and the total moment  $J = 8$ . The corresponding numbers for  $\text{Dy}^{3+}$  (9 electrons in the 4f-shell) are:  $S = \frac{5}{2}$ ,  $L = 5$ ,  $J = \frac{15}{2}$ . Thus, both values of  $J$  are rather large and close to each other.

All the compounds ( $R = \text{Y, La, Ho, Dy, Tm, Tb, Er, Yb}$ ) crystallize as perovskites with the rare earth ions forming a tetragonal centered lattice<sup>9</sup>. The magnetic moments of the Ho and Dy compounds are confined presumably in the  $ab$ -plane thus realizing the situation discussed above. The simplest crystal electric field (CEF) Hamiltonian  $H_{\text{CEF}}$  displaying tetragonal symmetry reads:

$$H_{\text{CEF}} = \frac{a}{2} J_z^2 - 2b(J_x^4 + J_y^4). \quad (7)$$

with  $a, b > 0$ . Quartic (and higher) terms in  $J_z$  are neglected since we assume  $J_z \ll J_x, J_y$ . For the same reason one can introduce the coordinate  $\varphi$  in a slightly simplified way (compared to (2)):  $J_x = J \cos \varphi$ ,  $J_y = J \sin \varphi$ , and  $J_z = -i\partial/(\partial\varphi) + A_\varphi$  with  $A_\varphi = 0$  for integer  $J$  and  $A_\varphi = 1/2$  for half-integer  $J$ . Together with the magnetic field contribution, the total Hamiltonian becomes:

$$H = -\frac{a}{2} \left( \frac{\partial}{\partial \varphi} - iA_\varphi \right)^2 - \frac{b}{2} J^4 (3 + \cos(4\varphi)) - hJ \cos(\varphi - \varphi_h), \quad (8)$$

where  $\varphi_h$  is the angle the magnetic field forms with the  $x$ -axis. The effective field  $h$  is the magnetic field times  $g\mu_B$ . The Hamiltonian (8) was found in a previous work<sup>12</sup> in which it was also analyzed for integer  $J$ .

It will be shown later that the CEF constants  $a$  and  $bJ^2$  are of the same order of magnitude. Due to the large value of  $J$  the potential energy has very deep minima near the points  $\varphi = \varphi_l = l\pi/2$ ,  $l \in \{0, 1, 2, 3\}$ . Let us denote the oscillatory states localized near each value of  $\varphi_l$  as  $|l\rangle$ . To be more specific, each  $|l\rangle$  is the groundstate<sup>13</sup> of  $H_l = -(a/2)\partial^2/(\partial\varphi^2) + U_l(\varphi)$  with

$$U_l(\varphi) = \begin{cases} -\frac{bJ^4}{2}(3 + \cos(4\varphi)) & \text{for } |\varphi - \frac{l\pi}{2}| \leq \frac{\pi}{4} \\ 2bJ^4 & \text{otherwise} \end{cases} \quad (9)$$

Without loss of generality we assume that the corresponding eigenenergy is zero. Neglecting the overlap between different  $|l\rangle$ , we find that the energy level is four-fold degenerate. The overlap lifts partly the degeneracy even in the absence of magnetic field. In complete analogy to the derivation of the dispersion of a tight-binding model<sup>14</sup> we define the hopping matrix element

$$w = -\langle l|H - H_{l+1}|l+1\rangle > 0. \quad (10)$$

The hopping part of effective Hamiltonian is

$$H_w = -w(C(\alpha) + C^+(\alpha)) \quad (11)$$

where  $C$  is the unitary rotation operator which induces  $|l\rangle \rightarrow |l+1\rangle \exp(i\alpha)$  and  $|3\rangle \rightarrow |0\rangle \exp(i\alpha)$ . For integer spin we have  $\alpha = 0$ , for half-integer spin we use  $\alpha = \pi/4$  resulting from

$$\exp(i\alpha) = \exp\left(i \int_{l\pi/2}^{(l+1)\pi/2} A_\varphi d\varphi\right). \quad (12)$$

This is the direct effect of the connection  $A_\varphi$  in absolute analogy to the Peierls phase in tight-binding models in magnetic fields. For what follows it is important to note that  $w$  is exponentially small if the wells at  $\varphi_l$  are deep enough such that the ground states  $|l\rangle$  are well, i.e. exponentially, localized. To estimate  $w$  we use the ansatz  $|l\rangle \propto \exp(-|\int_{l\pi/2}^\varphi \sqrt{2(U_l(\varphi) - U_{\min})/ad\varphi}|)$  which is motivated by the groundstate for the harmonic potential close to the minima and its natural extension in a WKB-type approach. The main contribution to the  $\varphi$ -integral for  $w$  comes from the vicinity of  $\varphi = \pi/4$  for  $l = 0$  and leads to

$$w \propto \exp\left(-\sqrt{\frac{2bJ^4}{a}}\right). \quad (13)$$

The eigenstates and eigenvalues of (11) are easily read off since we deal with a translationally invariant,  $d = 1$ , four-site tight-binding model. Thus the eigenstates are characterized by some momentum  $k \in \{0, \pm\pi/2, \pi\}$

$$\psi_k = \frac{1}{2} \sum_{l=0}^3 \exp(ikl) |l\rangle. \quad (14)$$

The corresponding eigenenergies are

$$E_k = -2w \cos(k + \alpha) . \quad (15)$$

Thus for integer  $J$  ( $\alpha = 0$ ) there is a non-degenerate groundstate ( $k = 0, E_k = -2w$ ), two degenerate excited states ( $k = \pm\pi/2, E_k = 0$ ), and the highest excited state ( $k = \pi, E_k = 2w$ ). For half-integer  $J$  ( $\alpha = \pi/4$ ) both the groundstate and the excited state are doubly degenerate with ( $k = 0, -\pi/2, E_k = -\sqrt{2}w$ ) and ( $k = \pi/2, \pi, E_k = \sqrt{2}w$ ).

The main difference between integer and half-integer spin resides here in a different degeneracy of the ground states. Physically this difference becomes manifest, for instance, when a magnetic field  $h$  is applied. We first consider an in-plane field as in (8). For well-localized states  $|l\rangle$  such a magnetic field is site-diagonal with matrix elements

$$H_h = hJ \cos(l\pi/4 - \varphi_h) . \quad (16)$$

The eigenvalues of  $H_w + H_h$  can be given analytically. For integer spins and half-integer spins one finds, respectively

$$E_{\text{int}} = \pm \sqrt{2w^2 + \frac{\bar{h}^2}{2} \pm \sqrt{\left(2w^2 + \frac{\bar{h}^2}{2}\right)^2 - \bar{h}_x^2 \bar{h}_y^2}} \quad (17a)$$

$$E_{\text{hint}} = \pm \sqrt{2w^2 + \frac{\bar{h}^2}{2} \pm \bar{h} \sqrt{2w^2 + \frac{\bar{h}^2}{4} - \frac{\bar{h}_x^2 \bar{h}_y^2}{\bar{h}^2}}} . \quad (17b)$$

where we used  $\bar{h}$  as a shorthand for  $hJ$ . From (17) one obtains for the groundstate energies in the limit of small magnetic fields

$$E_{\text{int}} \approx -2w - h^2 J^2 / (4w) \quad (18a)$$

$$E_{\text{hint}} \approx -\sqrt{2}w - hJ/2 . \quad (18b)$$

As expected the correction is quadratic in the non-degenerate, integer  $J$  case, but linear in the degenerate, half-integer  $J$  case (as in the linear Stark-effect). So we have for integer  $J$  a finite  $T = 0$  susceptibility

$$\chi_{\text{plane}} = -g^2 \mu_B^2 (\partial E)^2 / (\partial h^2) = g^2 \mu_B^2 J^2 / (2w) . \quad (19)$$

For half-integer  $J$  the system shows a finite magnetic momentum

$$\mu = -g\mu_B \partial E / (\partial h) = g\mu_B J/2 \quad (20)$$

leading to a Curie susceptibility diverging for  $T \rightarrow 0$ . This constitutes an essential difference between integer and half-integer spin. For large magnetic fields, however, the difference vanishes since  $w$  becomes unimportant. Asymptotically one obtains for  $hJ \gg w$

$$E \approx \pm hJ \cos(\varphi_h); \pm hJ \sin(\varphi_h) \quad (21)$$

irrespective of whether  $J$  is integer or half-integer. This equation implies that the corresponding magnetic moments are directed along one of the four easy axes. This intermediate asymptotics is valid in the range  $w \ll hJ \ll bJ^4$  where our tight-binding treatment stays valid. At significantly larger  $h$  the saturation magnetic moment is directed parallel to the magnetic field. Comparing (20) and (21) we, find that the finite magnetic moment at low magnetic field for half-integer  $J$  is precisely half of its saturation value ( $9.8\mu_B$  for  $\text{Dy}^{3+}$ ; cf.  $10\mu_B$  for  $\text{Ho}^{3+}$  with integer  $J$ ).

Let us consider now the action of magnetic field along the  $z$ -axis. To do so we rewrite

$$\begin{aligned} \frac{a}{2} J_z^2 - hJ_z &= \frac{a}{2} \left( J_z - \frac{h}{a} \right)^2 - \frac{h^2}{2a} \\ &= \frac{a}{2} \left( -\frac{i\partial}{\partial\varphi} + A_\varphi - \frac{h}{a} \right)^2 - \frac{h^2}{2a} . \end{aligned} \quad (22)$$

From this we infer that the  $z$ -axis magnetic field adds a constant to the Hamiltonian and acts as if the connection  $A_\varphi$  is changed in the manner  $A'_\varphi = A_\varphi - h/a$ . Inserting  $A'_\varphi$  in (12) shows that the Peierls phase  $\alpha$  in (11) is changed like  $\alpha \rightarrow \alpha - \pi h/(2a)$ . The effect of the Peierls phase change on the eigenenergies and on the groundstate energy in particular is easily found in (15). So, for integer  $J$ , we have  $E = -2w \cos(\pi h/(2a)) - h^2/(2a)$  and from this  $\chi_{\text{axis}} = a^{-1} - \pi^2 w/(2a^2)$ . Due to the exponential smallness of  $w$  (see (13)) the second term is negligible compared to the first one and we find  $\chi_{\text{axis}} = a^{-1}$  for integer  $J$ . Note that  $\chi_{\text{axis}}$  is exponentially small compared to  $\chi_{\text{plane}}$  in (19) which proves the consistency of our treatment for which we assumed that the moments are essentially confined to the plane. For half-integer spin we consider  $E = -2w \cos(\pi h/(2a) - \pi/4) - h^2/(2a)$  and derive  $\mu = -g\mu_B \partial E / (\partial h) = g\mu_B w/(\sqrt{2}a)$  for the local moment in  $z$ -direction. We obtain again a moment in  $z$ -direction which is exponentially small compared to the one in the plane (20) consistent with the outset of our theory. We observe that the difference between integer and half-integer  $J$  is also visible in the magnetic properties perpendicular to the easy plane.

The quasi-classical treatment implying the splitting of each oscillatory level into a quadruplet is valid provided that the level spacing between the localized oscillatory levels  $\omega$  is much larger than  $w$ . It is certainly incorrect for energies  $E$  close to the maximum potential energy  $U_{\text{max}} = 2bJ^2$ . One should have a rough idea on how many quadruplets our treatment can be expected to apply to. In the cases of interest  $J = 15/2, 8$  the total number of states is 16 or 17. Thus one can expect that one or two quadruplets are well described by the effective four-site tight-binding model. This conclusion is confirmed by direct diagonalization of the  $17 \times 17$  matrix in a model crystal field<sup>15</sup>. In order to have an estimate for the ratio  $b/a$  we compare the total number of states  $2J + 1$  with the number of levels  $N$  in the four wells of the poten-

tial  $U(\varphi) = -(bJ^4/2)(3 + \cos(4\varphi))$  in the quasi-classical approach

$$N = \frac{8}{\pi\hbar} \int_0^{\pi/4} \sqrt{2m(U_{\max} - U(\varphi))} d\varphi = \sqrt{\frac{32bJ^4}{\pi^2 a}}. \quad (23)$$

The area in phase space of the maximum classical orbit is divided by  $2\pi\hbar$  to obtain an estimate for the number of states. Here  $\hbar^2/m$  is set to  $a$ . Equating  $N$  to  $2J+1 \approx 2J$ , we find  $bJ^2/a = \pi^2/8 \approx 1.23$ , i.e. they are of the same order of magnitude.

Let us discuss the experimental consequences of the difference between integer and half-integer  $J$  described above. The clearest manifestations would occur in dilute alloys of Ho and Dy in the compounds  $\text{Lu}_{1-x}\text{Ho}_x\text{Ni}_2\text{B}_2\text{C}$ ,  $\text{Lu}_{1-x}\text{Dy}_x\text{Ni}_2\text{B}_2\text{C}$  or in similar alloys with Y in place of Lu. Both  $\text{Lu}^{3+}$  and  $\text{Y}^{3+}$  have zero magnetic moment. The direct check of our prediction would be the measurement of EPR spectra for these alloys at low temperature  $T < w$  (at about 2K according to the estimate in<sup>15</sup>). We expect that the lowest four levels are split as described above into singlet, doublet and singlet for Ho. The resonance frequency will not depend much on the magnetic field as long as  $\hbar J \ll w$ . In the case of Dy-alloys, however, the EPR resonance frequency is proportional to the magnetic field as long as this is small due to the finite magnetic moment. One can also check the nonlinear dependence of energies (17a, 17b) on the magnetic field.

Another option is to measure the magnetic field at a nucleus by NMR. The magnetic field at a nucleus must be essentially zero for Ho-alloys and non-zero for Dy-alloys.

Finally, one can also measure the spin magnetic susceptibility of the alloys at low temperatures. It should be constant  $(g\mu_B J)^2/(2w)$  per ion in the Ho-alloys. In the Dy-alloys, an in-plane Curie susceptibility  $(g\mu)^2/(3T) \approx (25g^2\mu_B^2)/(3T)$  per ion is expected due to the magnetic moments. Unfortunately, the paramagnetic effect will be strongly masked by the Meissner susceptibility  $\chi_M = -1/(4\pi)$  due to superconducting currents. One can, however, observe a remarkable weakening of the Meissner susceptibility at the temperature  $\sim 0.1\text{K}$  for concentrations of Dy of about 1%. At slightly lower temperatures the Dy-alloys must go over into a spin-glass state. No such transition can be observed in the Ho-alloys.

In conclusion, we have shown that the well-known difference between the magnetic properties of ions of integer or half-integer total magnetic moments  $J$  due to the absence or presence of Kramers degeneracy is captured in the quasi-classical limit of large  $J$  by a Berry phase. In the tetragonal environment studied here, integer spins display no finite magnetic moment in the groundstate, whereas the half-integer spins display a finite magnetic moment of half their saturation value. The difference is due to Kramers degeneracy<sup>7</sup> necessarily associated with half-integer spins. Any quasi-classical approach has to take the geometric Berry phase into account in order to capture the essential difference between integer and half-integer spin. The difference should be

manifest in the spectrum of EPR, NMR and in the magnetic susceptibility of dilute the alloys  $\text{Lu}_{1-x}\text{Ho}_x\text{Ni}_2\text{B}_2\text{C}$  and  $\text{Lu}_{1-x}\text{Dy}_x\text{Ni}_2\text{B}_2\text{C}$ .

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